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(54) UV-CURABLE RESIN COMPOSITION

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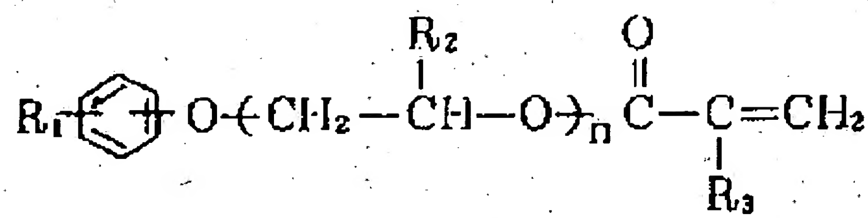
CLAIM

A UV-curable resin composition characterized by containing (A) a compound represented by the general formula [I]:



[I]

(in the formula, R_1 represents a hydrogen atom or a hydrocarbon group of 1-15 carbon atoms, R_2 and R_3 represent hydrogen atoms or methyl groups and n is on the average 5-15); (B) a polyurethane acrylate; and (C) a photopolymerization initiator.

DETAILED EXPLANATION OF THE INVENTION

INDUSTRIAL APPLICATION FIELD

The present invention concerns UV-curable resin compositions, and especially concerns UV-curable resin compositions for covering optical glass fibers for light transmission.

CONVENTIONAL TECHNOLOGY

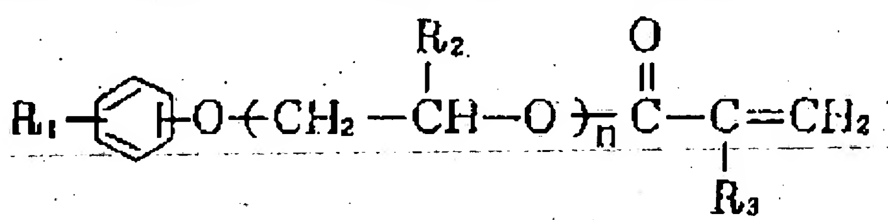
Optical glass fibers used for light transmission are brittle and easily scratched, lack flexibility, and are easily broken by slight external force. Therefore, conventionally, optical glass fibers are prepared from glass rods and immediately coated with a resin on the surface. For such resin coating materials, conventionally, epoxy resins, urethane resins, etc., have been used.

PROBLEMS TO BE SOLVED BY THE INVENTION

However, such resins require a long time for curing, resulting in poor productivity and lack of flexibility, thus transmission characteristics can be damaged by slight pressure.

MEANS FOR SOLVING THE PROBLEMS

As a result of an intense study for overcoming such problems, we have succeeded in providing novel UV-curable resin compositions suitable for coating on optical glass fibers for light transmission. The compositions have a fast curing rate, giving flexible coatings with a low glass transition temperature. Namely, the present invention concerns UV-curable resin compositions containing (A) a compound represented by the general formula [I]:



[I]

(in the formula, R_1 represents a hydrogen atom or a hydrocarbon group of 1-15 carbon atoms, preferably 8-12 carbon atoms and R_2 and R_3 represent hydrogen atoms or methyl groups; n is on the average 5-15); (B) a polyurethane acrylate; and (C) a photopolymerization initiator.

The compounds represented by the general formula [I] can be obtained by the esterification of (meth)acrylic acid with an adduct of an alkylphenol derivative and ethylene oxide or propylene oxide. In a specific example of making such compounds represented by the general formula [I], 1 mol of an adduct of an alkylphenol with ethylene oxide or propylene oxide, 1.0-2.0 mol, preferably 1.1-1.5 mol, of (meth)acrylic acid, an esterification catalyst (e.g., p-toluenesulfonic acid), and hydroquinone in an amount corresponding to 0.01-5 wt% with respect to the (meth)acrylic acid are heated together at 70-130°C, dewatered, washed with an alkali and washed with water to remove low-boiling substances to obtain a compound represented by the general formula [I]. Specific examples of the adducts of the alkylphenol derivative with ethylene oxide or propylene oxide used for making compounds of the general formula [I] include adducts of ethylene oxide or propylene oxide with alkylphenol derivatives such as phenol, cresol, tert-butylphenol, nonylphenol, octylphenol, dodecylphenol, etc.

The polyurethane acrylates (B) used in the present invention usually have a molecular weight exceeding 2000, preferably 3000-10000. Such polyurethane acrylates include polyurethane acrylates made from polyether polyols having ether groups in the molecule, polyurethane acrylates made from polyester polyols having ester groups in the molecule, polyurethane acrylates having both ether groups and ester groups, etc. The polyether polyols may be, e.g., adducts of ethylene oxide or propylene oxide with polyethylene glycol, polypropylene glycol, polytetramethylene glycol, 1,3-butylene glycol, 1,4-butylene glycol, 1,6-hexanediol, neopentyl glycol, cyclohexanedimethanol, 2,2-bis(4-hydroxycyclohexyl)propane, bisphenol A, etc. The polyester polyols can be obtained by reacting alcohols and acids. For example, adducts of ethylene oxide or propylene oxide with polyethylene glycol, polypropylene glycol, polytetramethylene glycol, 1,3-butylene glycol, 1,4-butylene glycol, 1,6-hexanediol, neopentyl glycol, cyclohexanedimethanol, 2,2-bis(4-hydroxycyclohexyl)propane, bisphenol A, etc., and ε-caprolactone adducts are used as the alcohol components; dibasic acids such as adipic acid, sebacic acid, azelaic acid, dodecanedicarboxylic acid, etc., and acid anhydrides made therefrom are used as the acid components. Reaction products from the above alcohol components and acid components as well as ε-caprolactone can also be used as the polyester polyols. For obtaining polyurethane acrylates (B) using such polyether polyols and polyester polyols, it is required to react the hydroxy groups of the polyols, organic isocyanates, and hydroxy-group-containing polymerizable monomers to reach complete disappearance of the NCO groups. Representative examples of the organic isocyanates include aromatic diisocyanates such as tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, etc.; alicyclic

diisocyanates such as isophorone diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, etc.; aliphatic diisocyanates such as hexamethylene diisocyanate, 2,2'-trimethylhexamethylene diisocyanate, etc. The hydroxy-group-containing polymerizable monomers include hydroxy-group-containing (meth)acrylates, etc., such as β-hydroxyethyl (meth)acrylate, β-hydroxypropyl (meth)acrylate, β-hydroxylauryl (meth)acrylate, ε-caprolactone adduct with β-hydroxyethyl (meth)acrylate, etc. The reaction between the NCO groups and OH groups can proceed without catalysts, while the usual catalysts such as tertiary amines like triethylamine, etc., organometallic compounds such as dibutyltin dilaurate, dibutyltin diacetate, etc., tin chlorides, etc., can be used. Based on 100 parts by weight of the compounds represented by the general formula [I], the amount of polyurethane acrylate (B) used should be below 200 parts by weight. An excessive amount would raise the viscosity, making handling difficult. The photopolymerization initiators (C) used in the present invention can be chosen from commonly known photopolymerization initiators, while a good storage stability after being compounded is required. Such photopolymerization initiators are, e.g., benzoin alkyl ethers such as benzoin ethyl ether, benzoin isobutyl ether, benozin isopropyl ether, etc.; acetophenones such as 2,2-diethoxyacetophenone, 4'-phenoxy-2,2-dichloroacetophenone, etc.; propiophenones such as 2-hydroxy-2-methylpropiophenone, 4'-isopropyl-2-hydroxy-2-methylpropiophenone, 4'-dodecyl-2-hydroxy-2-methylpropiophenone, etc.; benzil dimethyl ketal; 1-hydroxycyclohexyl phenyl ketone; anthraquinones such as 2-ethylanthraquinone, 2-chloroanthraquinone, etc., ; thioxanthones, etc. Such photopolymerization initiators (C) may be used alone or as mixtures thereof. The amount of the catalysts used is usually 0.1-10 wt% with respect to the resin compositions. If needed, the UV-curable resin compositions of the present invention may also contain polymerizable monomers including monofunctional unsaturated monomers such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, polybutylene glycol mono(meth)acrylate, ε-caprolactone-β-hydroxyethyl (meth)acrylate adducts (Placcel FA-1 and Placcel FM-1, products of Dai-Cel Kagaku Kogyo Co.), tetrahydrofurfuryl alcohol-ε-caprolactone adduct (meth)acrylate (Kayarad TC-110S, Kayarad TC-120, etc., products of Nippon Kayaku Co.); N-difunctional unsaturated compounds such as polyethylene glycol di(meth)acrylate, polypropylene glycol di(meth)acrylate, etc. Also, if needed, modifying resins and various additives can be added. The modifying resins may be epoxy resins, polyurethanes, polybutadiene, polyethers, polyamide-imides, silicone resins, phenolic resins, etc., and the additives may be organosilicon compounds, surfactants, polymerization inhibitors, antioxidants, etc.

APPLICATION EXAMPLES

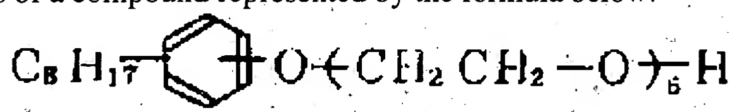
Next, the present invention is explained in further detail with application examples.

In the examples, parts are by weight.

Examples for making compounds (A) represented by the general formula [I]:

MANUFACTURING EXAMPLE 1

In a 2-L reactor fitted with a stirrer, a temperature control device, a thermometer, and a condenser, 300 parts of a compound represented by the formula below:

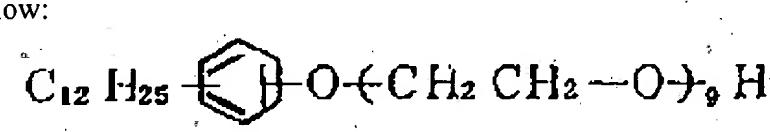


55.1 parts of acrylic acid, 10 parts of p-toluenesulfonic acid, 0.5 part of hydroquinone, 320 parts of benzene, and 80 parts of cyclohexane were added and heated, during which the water formed was distilled off together with the solvent, condensed, and sent through a separator to remove only water from the reaction system, then recycling of the solvent into the reaction system. When water formation reached 11.5 parts, the reaction mixture was cooled. The reaction temperature was 82-88°C. The reaction mixture was dissolved in a mixture of 480 parts of benzene and 120 parts of cyclohexane, neutralized with a 20% sodium hydroxide aqueous solution, washed three times with 300 parts of a 20% sodium chloride solution, and freed from the solvent by vacuum distillation to obtain 273 parts of a light yellow liquid having the properties shown below:

Specific gravity (25°C)	1.05
Viscosity (25°C)	160 cps [cP]
Saponification value	105.9 mg KOH/g
Acid value	0.04 mg KOH/g
Refractive index (20°C)	1.4940

MANUFACTURING EXAMPLE 2

In the reactor used in the Manufacturing Example 1, 658 parts of a compound represented by the formula below:



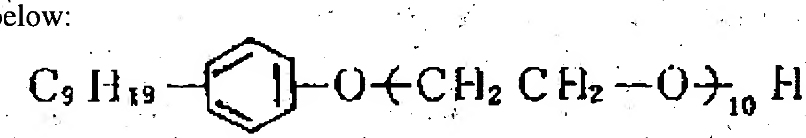
86.5 parts of acrylic acid, 10 parts of p-toluenesulfonic acid, 0.7 part of hydroquinone, 480 parts of benzene, and 120 parts of cyclohexane were added and reacted similarly as in Manufacturing Example 1. When water formation reached 18 parts, the reaction mixture was cooled. The reaction mixture was dissolved in a mixture of 848 parts of benzene and 212 parts of

cyclohexane, neutralized with a 20% sodium hydroxide aqueous solution, washed three times with 300 parts of a 20% sodium chloride solution, and freed from the solvents by vacuum distillation to obtain 569.6 parts of a light yellow liquid having the properties shown below:

Specific gravity (25°C)	1.039
Viscosity (25°C)	266 cps
Saponification value	76.5 mg KOH/g
Acid value	0.05 mg KOH/g
Refractive index (20°C)	1.04885

MANUFACTURING EXAMPLE 3

In the reactor used in the Manufacturing Example 1, 660 parts of a compound represented by the formula below:

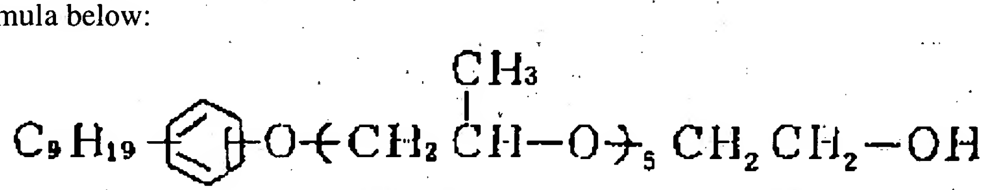


86.5 parts of acrylic acid, 10 parts of p-toluenesulfonic acid, 0.7 part of hydroquinone, 480 parts of benzene, and 120 parts of cyclohexane were added and reacted similarly as in Manufacturing Example 1. When water formation reached 18 parts, the reaction mixture was cooled. The reaction mixture was dissolved in a mixture of 848 parts of benzene and 212 parts of cyclohexane, neutralized with a 20% sodium hydroxide aqueous solution, washed three times with 400 parts of a 20% sodium chloride solution, and freed from the solvents by vacuum distillation to obtain 592 parts of a light yellow liquid having the properties shown below:

Specific gravity (25°C)	1.065
Viscosity (25°C)	218 cps
Saponification value	77.4 mg KOH/g
Acid value	0.04 mg KOH/g
Refractive index (20°C)	1.4885

MANUFACTURING EXAMPLE 4

In the reactor used in the Manufacturing Example 1, 554 parts of a compound represented by the formula below:



86.5 parts of acrylic acid, 10 parts of p-toluenesulfonic acid, 0.7 part of hydroquinone, 400 parts of benzene, and 100 parts of cyclohexane were added and reacted similarly as in Manufacturing

Example 1. When water formation reached 18 parts, the reaction mixture was cooled. The reaction mixture was dissolved in a mixture of 1024 parts of benzene and 256 parts of cyclohexane, neutralized with a 20% sodium hydroxide aqueous solution, washed three times with 300 parts of a 20% sodium chloride solution, and freed from the solvents by vacuum distillation to obtain 460 parts of a light yellow liquid having the properties shown below:

Specific gravity (25°C)	0.9968
Viscosity (25°C)	144 cps
Saponification value	89.5 mgKOH/g
Acid value	0.05 mgKOH/g
Refractive index (20°C)	1.4800

Examples for making polyurethane acrylates (B)

MANUFACTURING EXAMPLE 5

In a 2-L reactor fitted with a stirrer, a temperature control device, a thermometer, and a condenser, 253.1 parts of polypropylene glycol (molecular weight about 2000, OH value 56.1), 251.3 parts of a polyester polyol made from neopentyl glycol adipic acid and ε-caprolactone (product of Dai-Cel Kagaku Kogyo Co., Placcel L-220AL, molecular weight about 2000, OH value 57.5), and 74.8 parts of isophorone diisocyanate were added, then reacted by heating at 80°C for 10 h, and allowed to cool to 60°C; 61.7 parts of ε-caprolactone-β-hydroxyethyl acrylate (product of Dai-Cel Kagaku Kogyo Co., Placcel FA-2), 0.3 part of methoquinone, and 0.1 part of di-n-butyltin dilaurate were added then reacted at 75-80°C until the free isocyanate group content reached below about 0.1%. The product had the following properties:

Viscosity (60°C)	185 P
Refractive index (20°C)	1.4715

MANUFACTURING EXAMPLE 6

In the same reactor used in Manufacturing Example 5, 787.36 parts of polytetramethylene glycol (molecular weight about 2000, OH value 57) were added and heated to 60°C; 131.8 parts of tolylene diisocyanate were then added dropwise, reacted by heating at 80°C for 10 h, and allowed to cool to 60°C; 81.9 parts of 2-hydroxyethyl acrylate, 0.5 part of methoquinone, and 0.19 part of di-n-butyltin dilaurate were added and reacted at 80°C to obtain a hydroxyethyl acrylate adduct with a polytetramethylene glycol-tolylene diisocyanate adduct as the reaction product having the following properties:

Viscosity (60°C)	257.5 P
Refractive index (20°C)	1.4850

MANUFACTURING EXAMPLE 7

In the same reactor used in Manufacturing Example 5, 404.3 parts of polypropylene glycol (molecular weight about 1000, OH value 111 mg KOH/g) were added and heated to 60°C; 104.4 parts of tolyene diisocyanate were then added dropwise and reacted by heating at 80°C for 10 h, and allowed to cool to 60°C; 51.05 parts of 2-hydroxyethyl acrylate, 0.28 part of methoquinone, and 0.11 part of di-n-butyltin dilaurate were added and reacted at 80°C obtain a hydroxyethyl acrylate adduct with a polypropylene glycol-tolylene diisocyanate adduct as the reaction product having the following properties:

Viscosity (60°C)	60 P
Refractive index (20°C)	1.4890

Examples of UV-curable resin compositions:

APPLICATION EXAMPLE 1

A resin composition (coating material) A was prepared by mixing 50 parts of the polymerizable monomer obtained in Manufacturing Example 2, 10 parts of phenoxyethyl acrylate, 40 parts of polyurethane acrylate obtained in Manufacturing Example 5, 5 parts of 1-hydroxycyclohexyl phenyl ketone (product of Ciba-Geigy Co., Irgacure 184), and 0.01 part of methylhydroquinone. The composition properties are shown in Table I.

APPLICATION EXAMPLE 2

A resin composition B was prepared by mixing 20 parts of the polymerizable monomer obtained in Manufacturing Example 1, 30 parts of the polymerizable monomer obtained in Manufacturing Example 4, 10 parts of ε-caprolactone-β-hydroxyethyl acrylate (product of Dai-Cel Kagaku Kogyo Co., Placcel FA-2), 40 parts of polyurethane acrylate obtained in Manufacturing Example 6, 5 parts of 1-hydroxycyclohexyl phenyl ketone, and 0.01 part of methylhydroquinone. The composition properties are given in Table I.

APPLICATION EXAMPLE 3

A resin composition C was prepared by mixing 40 parts of the polymerizable monomer obtained in Manufacturing Example 1, 10 parts of ε-caprolactone-β-hydroxyethyl acrylate, 50 parts of the polyurethane acrylate obtained in Manufacturing Example 7, 5 parts of 4'-dodecyl-2-hydroxy-2-methylpropiophenone (product of Merck Co., Darocure 953), and 0.01 part of methylhydroquinone. The composition properties are given in Table I.

APPLICATION EXAMPLE 4

A resin composition D was prepared by mixing 65 parts of the polymerizable monomer obtained in Manufacturing Example 3, 35 parts of the polyurethane acrylate obtained in Manufacturing Example 5, 5 parts of Darocure 953, and 0.01 part of methylhydroquinone. The composition properties are given in Table I.

COMPARATIVE EXAMPLE

A resin composition E was prepared by dissolving 5 parts of 2-ethyl-4-methylimidazole in 100 parts of an epoxy resin Epikote 828 (product of Shell Oil Co.). The composition properties are given in Table I.

Table I

	Resin compositions (coating materials)				
	A	B	C	D	E
Viscosity (cps/25°C)	3400	4400	2800	3000	15000
Curing time (sec/150°C)	-	-	-	-	59
Curing time (sec/mercury lamp 80 W/cm)	0.2	0.2	0.2	0.2	-
Hardness (Shore A)	40	53	52	42	>100
Glass transition temperature (°C)	-47.1	-53.4	-35.4	-55.4	115

In the Table I:

Curing time measurement

For compositions A, B, C, and D, irradiation was conducted using a high-pressure mercury lamp (input 80 W/cm, lamp output 2 kW) as the light source positioned parallel 8 cm above the coating (conveyer speed of 50 m/min) on glass in N_2 gas; the time needed for the coating surface to become tack-free is given in the table. For the composition E, the gelation time at 150°C is given.

Shore A hardness measurement

For compositions A, B, C, and D, 250-μm-thick sheets were prepared by irradiation with a high-pressure mercury lamp (input 80 W/cm, lamp output 2 kW) as the light source positioned parallel 8 cm above the coating (conveyer speed of 50 m/min) and measured. For the composition E, measurement was made for a 2-mm-thick plate cured at 150°C for 15 min.

Glass transition point

Measurements were made for test plates obtained similarly as in the above Shore A hardness measurement.

EFFECTS OF THE INVENTION

The UV-curable resin compositions of the present invention have low viscosity and give flexible resin coatings with a fast curing speed and low glass transition point; thus they are suitable for coatings for optical glass fibers used for light transmission.